A

Synopsis On

A Computational Probe on Aggregation And Stacking In NIR Absorbing Organic Functional Materials

Submitted by

Ms. Rupali Raosaheb Deshmukh

to

Swami Ramanand Teerth Marathwada University, Nanded,

Maharashtra, India

In partial fulfillment of registration to

Doctor of Philosophy in Chemistry

Under the faculty of

Science and Technology

Under the Guidance of

Dr. G. Krishna Chaitanya

Associate Professor,

School of Chemical Sciences,

Swami Ramanand Teerth Marathwada University, Nanded.

Sept 2023

1. Origin of the Proposal:

Supramolecular interactions and aggregation behaviour of functional materials attained great importance to tune and extend their spectral sensitivity and, hence, improve the optoelectronic response of related devices [1]. Thus, the studies on crystallisation and aggregation behaviour of a variety of organic functional materials have become an important topic in recent years [2-8].

The optical properties and aggregation behaviour of squaraine (SQ) dyes have attracted a wide research interest in recent years, owing to their promising application in dye-sensitised [9-11], organic [12-13] and perovskite solar cells [14], organic light-emitting diodes (OLEDs) [15] and biomedical applications [16-17]. Conventionally, SQ dyes are known as quadrapolar type of donor-acceptor-donor (D-A-D) systems with electron rich side substituents as donor and core group (central four-membered ring and the carbonyl oxygens) as acceptors. Also, SQ exhibits a highly rigid and planar structure, and has a strong tendency to aggregate, which can significantly affect their charge transport ability in optoelectronic devices [18–22].

SQ dyes show a strong tendency to form both J-type and H-type aggregates in solution, which possess significant bathochromic and hypsochromic shift respectively compared to the monomeric band [7]. On the other hand, in solid state, the presence of polymorphic species that includes the coexistence of J-, H- and oblique aggregates that lead to a splitting of the absorption band into two components around the monomer absorption, results Davydov splitting [22-26]. However, understanding the relationship between aggregate structure- property relationship for SQ dyes is not yet established completely.

On the other hand, in a recent report, aggregates of quadrupolar D-A-D type chromophores have been investigated theoretically using the essential states model (ESM) [29]. It is highlighted that quadrupolar dye aggregates can exhibit highly unconventional red-shifted H-aggregate (non-Kasha) spectroscopic behaviour, driven by the large quadrupole−quadrupole interactions. This implicates the need of full understanding of the intermolecular interactions in order to effectively design the molecular structure for optimal performance in device applications.

Hence, in this proposal, the detailed computational study of intermolecular interactions at stacking/aggregation level in the quadrapolar SQ systems has been considered which will help the understanding of structure-properties relationships for potential materials applications.

2. Review of status of Research and Development in the subject

2.1 International Status:

Much extent, research work has been progressed in the area of organic functional materials related to SQ dye derivatives. However, to limit with, some of the recent studies on specifically to aggregation and crystal packing patterns found materials application have been presented here.

Christopher J. Collison *et al* have successfully explained the interplay between monomer SQ and its respective aggregate in spin cast thin films that has provided another dimension to have control on the charge mobilities on organic photovoltaics [31]. The broad and double-peaked nature of the absorption spectra of aggregates and thin films of the SQ dyes is due to intermolecular charge transfer has also been reported from the same group. The limitation of explaining the spectra by conventional exciton theory in terms of H- and J-aggregation as originally proposed by Kasha is explored [32]. Similarly G. M. Paterno *et al* have investigated the absorption/emission properties of a single SQ aggregate by confocal microscopy, UV-Vis and PL spectroscopy and elucidated the role of H- and J-aggregates in the same [33].

In general, more the crystalline the thin film is, expected to show improved charge carrier and exciton transport. However, the material characterization and single crystal X-ray analysis of bis(3,5-dimethyl-1H-pyrrol-2-yl)-3-oxocyclobut-1-en-1-olate (PSQ) and a derivative of this symmetric SQ dye with a thiophene substituent (NSP) showed that the vacum deposited PSQ film is largely amorphous and the NSP film is more crystalline. Interestingly, the amorphous PSQ film has got significantly superior performance in organic photovoltaics with respect to crystalline NSP film. This strnage behavior has been attributed to the more efficient exciton transfer between amorphous PSQ and C_{60} [34].

In an another report, the incorporation of end capping with electron withdrawing -CN group has altered greatly the magnitude of dipole moment which resulted more compact crystal packing with enhanced intermolecular dipole-dipole interactions and so the higher hole mobility than the unsubstituted SQ derivative is presented [35].

On the other hand, the impact of different terminal functionalization of SQ on aggregation behaviour and, consequently, their optoelectronic solid state properties including charge carrier mobility and finally the solar cell performance are investigated [36]. This demonstrates not only the versatility of SQ in photovoltaic applications, but shows also the possibility of controlling the device performance by simple structural tuning of the molecular building blocks. In a report, a series of aniline based SQ derivatives with variable side alkyl chain substitutents have been studied for BHJ and OPV devices. This study provides a rational design principle based on the crystal packing and resulting intermolecular interactions affected by the length of alkyl chain [37]. To be noted, interestingly, aniline based SQ derivative with branched iso-butyl side substitutions has got two polymorphs i.e. Monoclinic and orthorhombic in bulk and spin casted films respectively. Both polymorphs adopt herringbone packing, the monoclinic phase comprising coplanar and slipped molecular stacks, and the orthorhombic phase exhibiting oblique angled molecular stacks with alternating twist. The correlation of Structure, morphology, molecular orientation, and excitonic optical properties in polymorphic thin films has been established [38].

In case of unsymmetrical SQ (USQ) derivatives, the significance of coulomb interactions in BHJ organic solar cells has been studied with the help of three USQ dyes and concluded that the extent of intermolecular coulomb interactions play a key role in mobility of charge carriers [39]. Also, the role of

extended conjugation in intermolecular π-π interactions in photophysical, thermal, electrochemical and semiconducting properties of OFET designed with USQ derivatives has been reported [40].

On the other hand, the substitution of dicyanomethylenation on the central squaric acceptor core (CSQ) will lead to distinctly altered properties on the entire π-conjugated system of the fluorophore, such as lowering of the optical bandgap, stabilizing the HOMO level, increasing the dipole moment and change in the dipole moment direction. This facilitates much enhanced open-circuit voltage and significantly increased short-circuit current density, hence drastically higher PCEs than their corresponding USQ-based reference devices in small molecule BHJs [41].

In order to study the role of hetero atoms along with varying the length of alkyl substituents, a series of acceptor-substituted SQ with different donor moieties bearing -Se, -S, or -O atoms have been synthesized and studied for solution-processed transistor devices. Quite high hole mobility in orthogonal direction was explained by CN···Se interactions which constitute a new motif in the field of organic semiconductor research [42]

2.2 National Status:

In line with the research work progressed at international level on the incorporation of SQ derivatives in organic functional materials, lot of work has also been done at national level by various research groups. However, some of the recent reports have been presented here with respect to the context of the proposal.

Rajiv K. Singh *et al* (CSIR-NPL) have studied ultrafast charge carrier dynamics as well as the generation of polaron pair in SQ and SQ:[6,6]-phenyl-C 71-butyric acid methyl ester (SQ:PCBM71) using ultrafast transient absorption spectroscopy. This study reveals that the pure SQ exhibits the creation of singlet and triplet states (typical character of SQ derivatives); however, incorporation of PCBM71 results in the formation of polaron pairs with ⍰550ps lifetime, which leads to the creation of free electrons in the device [43].

Ganapati Shankarling et al (ICT, Mumbai) have successfully synthesized two novel acceptor–donor-acceptor-donor-acceptor (A2-D-A1-D-A2) type π-conjugated symmetrical SQ dyes for the first time to arrive absorption and emission at NIR region. The structure-property relationship of these dyes was studied in comparison with their parent compounds [44].

Another research group (S. P. Singh) from CSIR-IICT, has adopted a novel core and wings concept and designed SQ dyes end-capped with three different wings, such as malononitrile, 2-(3-hexyl-4-oxothiazo-lidin-2-ylidene)malononitrile, and 3-ethyl-2-thioxothiazolidin-4-one. From the sensitivity of absorption and emission spectra of these dyes, it is suggested that the excited state of all the SQ dyes is more polar than the ground state [45]. From the same group, multichromophoric USQ sensitizer via C-H arylation has been designed with thethieno[3,2-b]thiophene unit as π-spacer, dicyanovinyl and cyanoacrylic acid unit as acceptor which has potential for transparent solar cell application [46].

From Jayaraj Nithyanandhan's research group (CSIR-NCL), in order to control the aggregation of SQ dyes on TiO_2 surface, a series of fused indenoquinaldine based USQ derivatives have been synthesized and applied for DSSCs. They have achieved panchromatic IPCE response which ranges from 400 nm to 880 nm and efficient electron injection by the both H-type and J-type aggregates along with the monomers [47]. Similarly, a series of four USQ dyes, were synthesized using fused fluorenylindolenine

based donor unit for DSSCs. Introduction of branched alkyl groups on the π-framework helped in controlling dye aggregation to reduce exciton quenching and assisted in TiO_2 surface passivation to avoid the charge recombination process [48]. In another report, both steric and electronic factors have been considered and designed a series of cis-configured USQ dyes with suitably functionalized alkyl groups and electron withdrawing group for DSSCs. The controlled self- assembly of the dyes on the TiO_2 surface has been achieved which helps to broaden the absorption profile of the dyes with increased energy harvesting process [49].

The intramolecular exciton coupling was studied by Ajayaghosh's research group (CSIR-NIIST) by designing V-shaped SQ dyes with carbazole cores in the center and indolenine groups at the end to broaden the light-harvesting range of dye-sensitized solar cells (DSSCs). [50].

The computational studies by C. H. Suresh (CSIR-NIIST) offered the structural and electronic features of bis(4-dimethylamino-phenyl)squaraine studied by using density functional BLYP/ cc-pVTZ level of theory and confirmed the highly charge separated quadrupolar nature of the compound [51].

On the other hand, S.K.Pati and co-workers (JNCASR) adopted the ESM method to investigate small aggregates of quadrupolar (A-π-D-π-A or D-π-A-π-D) charge-transfer dyes by focusing the attention on the role of intermolecular interactions on optical properties. The approach was applied to curcuminoid and SQ dyes, with weak and strong quadrupolar character, respectively [52].

2.3 Importance of the proposed project in the context of current status

Of particular interest, the organic functional dyes have become the choice of researchers in material science due to their features such as flexibility, a high interaction with light, and most important, the ability to custom tailor the synthesis of the dye in an absorption range of choice. Here, computational chemistry based on quantum chemical theories, which are replacing the earlier empirical rules, is playing a major role in understanding the dyes post priori experiment or in suggesting modifications for the a priori synthesis suitable to the applications.

In support to our findings, recent experimental findings to enhance the photocurrent conversion efficiencies of symmetrical SQ derivatives with addition of chenodeoxycholic acid as coadsorbent are found [59-60]. The addition of coadsorbent suppresses the aggregation of dye and the obtained performance of symmetrical SQ derivatives is superior to USQ analogs besides slight bathochromic shift of the absorption and higher stability of the former. It was also shown that the anchoring as well as electron withdrawing –COOH moieties have little effect on lowest electron transition corresponding to π-π* electron transition, mainly localized on central SQ moiety. However, observed *cis* and *trans* conformational flexibility has major effect in attaining large charge polarization with *cis* type symmetrical SQ derivatives hence better charge injection takes place into conduction band of TiO_2 when compared with USQ analogs.

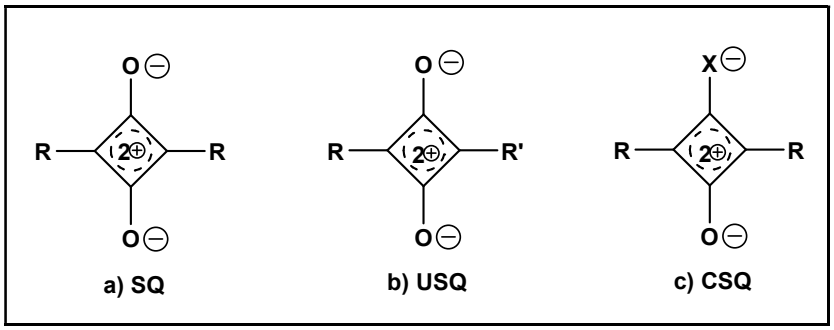
On the other hand, as mentioned in the origin of the proposal, the supramolecular interactions and aggregation behaviour of functional materials is of great importance to tune and extend their spectral sensitivity and, hence, improve the optoelectronic response of related devices. In this context, the quadrapolar SQ systems have been considered in this proposal to investigate the charge mobilities dependency on intermolecular interactions based on its stacking arrangements (H-, J- and combination of

both H and J) and dipole-dipole interactions. To be noted, the charge mobilities calculated through reorganization energies at molecular level are not so reliable and seldom discouraging too.

3. Work Plan:

3.1 Methodology:

Conventionally, SQ dyes are known as D-A-D dyes with electron rich side substituents as donor and core group (central four-membered ring and the carbonyl oxygens) as acceptors. Based on the structure, the SQ dyes can be categorized to three types, namely, symmetrical SQ (both donors are same), unsymmetrical SQ (USQ, different donors on both sides) and core substituted SQ (CSQ, substitution at central core group with electron withdrawing group) as shown in scheme 1.



Scheme 1: Representation of a) symmetrical SQ derivative, b) unsymmetrical SQ dye (USQ) derivative and c) core substituted SQ (CSQ) derivative.

As mentioned in the above sections, intermolecular interactions i.e. π-π stacking interactions (face-to-face/head-to-head/head-to-tail/side-to-side/substituted metal atom like Se to π-cloud), electrostatic interactions and van der waals interactions have become one of the key parameters to evaluate the charge mobility at the bulk level. Apart from this, various crystal packing modes have been reported with respect to the variation in alkyl chain lengths or reaction conditions. However detailed investigation was not performed to understand the correlation between electronic structure and charge carrier mobility. Few representative crystal packing modes of SQ, USQ and CSQ derivatives are given below.

<u>The specific objectives of the present proposal have been identified as:</u>

1. Though the variation of substituents on side electronic rich aromatic groups did not induce CT phenomenon at molecular level, its impact on intermolecular interactions has not been answered yet. This will be prime objective of this proposal.
2. Correlation between molecular orbital structure and crystal orbital structure to analyze the extent of intermolecular interactions and so the retention of biradicaloid OXA character in bulk phase.
3. Understanding the effect of alkyl chain substituents (along with its position) on the stacking and associated charge mobilities in the crystal phase.
4. If more than one stacking mode is feasible for a specific SQ derivative then understating the nature of interactions in the crystal phase.
5. Evaluating the effect of electron withdrawing substitution (-X) on stacking and comparing with its parent SQ/USQ derivatives.

6. Extending the computational results to design and synthesis new SQ derivatives by collaborating with experimental collaborators.

Computational Methodology:

The crystal structures will be obtained from the experimental reports and "The Cambridge Crystallographic Data Centre". They will be initially screened to identify the crystal packing patterns and crystallographic symmetry.

Based on the knowledge from the electronic structure of SQ derivatives at molecular level, comparison will be made between the molecular orbital and crystalline orbitals. As mentioned in previous sections, even the strong electron withdrawing groups like dicyanomethyl on central SQ moiety could not create deviation from the molecular orbital nature of parent unsubstituted SQ derivative [58]. Thus, this kind of correlation study will certainly help us to understand the extent of intermolecular interactions on crystal orbital structure.

At molecular level: The calculation of reorganization energies and charge transfer integrals for the crystal structures will be performed by using Gaussian16 software. Using the optimized neutral geometries, the internal reorganization energies based on Marcus theory are calculated at B3LYP/6-31+G (d,p) level of theory. Frequency calculations will be carried out for optimized cations and anion geometries to ensure that these stationary points are minima on the potential energy surface. Intermolecular interaction energies will be obtained using dispersion corrected B2PLYPD/6-31G(d,p) for all possible interactions at crystal level. Counterpoise corrected basis set superposition errors will be added to the interaction energies.

The reorganization energies for hole (λ_+) and electron (λ-) will be calculated by using equations 1 and 2, given below.

$$\lambda_+ = \lambda_1 + \lambda_2 \text{----------eq (1)}$$

$$\lambda_- = \lambda_3 + \lambda_4 \text{----------eq (2)}$$

Here the energy required (λ_1, eV) for the reorganization of the neutral geometry to the cation geometry upon removal of an electron added to the energy required (λ_2) to reorganize the obtained cation geometry back to a neutral state upon re-accepting an electron gives the total reorganization energy (λ+) of the molecule when the charge is being transported. In a similar fashion the reorganization energy (λ-) of the neutral to anion (λ_3) and back (λ_4) should be useful in understanding the electron transport.

Hole and electron drift mobilities will be calculated based on the hopping model where the charge hops between two neighboring molecules (i and j). The hole-transfer/electron-transfer reactions between the neighboring molecules is portrayed as

$$A^{+/-} + A \rightarrow A + A^{+/-} \quad \text{---------- eq (3)}$$

Where A is the neutral molecule interacting with neighboring oxidized (A^+) or reduced (A^-) molecule. The drift mobility of hopping μ, can be obtained from the Einstein relation

$$\mu = \frac{e}{K_b T} D \text{ ---------- eq (4)}$$

Where *e* is the electronic charge and D is the isotropic charge diffusion coefficient, kb is the Boltzmann constant, and T is the temperature.

According to Marcus theory, the rate constant for charge transfer (CT)/hopping rate is be defined as

$$k_i = \frac{4\pi^2 (J_{eff})_{ij}{}^2}{\mathrm{h}} \frac{1}{\sqrt{(4\pi\lambda k_b T)}} \mathrm{e}^{(-\lambda/4k_b T)} \quad \text{---------- eq (5)}$$

Where $(J_{eff})_{ij}$ is the effective charge transfer (hole/electron) transfer integral/coupling matrix element between neighboring molecules, λ is the reorganization energy (λ_+ for hole and λ_- for electron).

The effective charge-transfer integrals $(J_{eff})_{ij}$ for the hole and electron transfer will be estimated using the Entire Dimer Hamiltonian (EDH) method, for all the possible interaction pathways. The matrix elements of the molecular Kohn-Sham Hamiltonian in the basis of fragment orbitals are used to calculate site energies e_i and e_j and charge transfer integrals. Likewise the overlap integrals, S_{ij}, between fragment orbitals are calculated. The effective $(J_{eff})_{ij}$ is calculated using the following equation,

$$(J_{eff})_{ij} = \frac{J_{ij} - S_{ij}(e_i + e_j)/2}{1 - S_{ij}^2} \text{ ---------- eq (6)}$$

At crystal level: Crystal orbital overlap population (COOP) and crystal orbital Hamiltonian population (COHP) analysis allows for the investigation of electronic states within a material. The COOP/COHP calculation is specifically aimed at the interaction between two selected groups of orbitals/atoms. Thus, information regarding bonding and antibonding states, bond orders, and interaction strengths can be obtained in a straightforward fashion. The difference between the COOP and COHP analyses lie in the usage of either the overlap matrix (S) or the Hamiltonian matrix (H) elements for COOP and COHP, respectively. The former provides a measure of the bond order, while the latter a measure of bond strength.

All the crystal level calculations will be carried out by using composite methods for molecular crystals like HF-3c, PBEh-3c, HSE-3c and B97-3c methodologies with the periodic *ab-initio* CRYSTAL17 code. Crystalline orbitals can be represented as linear combinations of Bloch functions (BF), and are evaluated over a regular three-dimensional mesh in reciprocal space. Each BF is built from local atomic orbitals (AO), which are contractions (linear combinations with constant coefficients) of Gaussian-type functions (GTF), each GTF being the product of a Gaussian times a real solid spherical harmonic. All electron basis sets shall be used for main group elements and pseudo-potentials for heavy metal atoms. Severe convergence and general conditions shall be adopted for the calculation. The grid for the numerical integration of the exchange-correlation term can be employed with suitable radial and angular points in a Lebedev scheme with no symmetry constraints; hence a full relaxation of both lattice parameters and atomic coordinates will be performed. The total energy obtained with this mesh is fully converged. DFT-D3 correction for dispersive interactions will be considered to study the intermolecular interactions. As SQ derivatives possess the biradicaloid character, spin contamination correction will also be included. The total and projected density of states will be evaluated on the optimized geometries along with BAND projected states. The crystal orbital populations and electrostatic potentials will be evaluated.

References:

1. G. M. Paternò, L. Moretti, A. J. Barker, C. D'Andrea, A. Luzio, N. Barbero, S. Galliano, C. Barolo, G. Lanzani, F. Scotognella, ***J. Mater. Chem. C***, 2017,**5**, 7732-7738
2. W. Wang, A. Fu, J. Lan, G. Gao, J. You, L. Chen, ***Chemistry***, 2010, **16**, 5129-5137.
3. N. Narayanan, V. Karunakaran, W. Paul, K. Venugopal, K. Sujathan, K. Kumar Maiti, ***Biosensors & bioelectronics***, 2015, **70**, 145-152.
4. G. Paterno, A. J. Warren, J. Spencer, G. Evans, V. G. Sakai, J. Blumberger, F. Cacialli, ***J. Mater. Chem. C***, 2013, **1**, 5619-5623.
5. G. Tregnago, M. Wykes, G. M. Paterno, D. Beljonne, F. Cacialli, ***J. Phys. Chem. C***, 2015, **119**, 11846-11851.
6. J. Mei, Y. Hong, J. W. Lam, A. Qin, Y. Tang, B. Z. Tang, ***Advanced materials***, 2014, **26**, 5429-5479.
7. F. Wurthner, T. E. Kaiser, C. R. Saha-Moller, ***Angewandte Chemie***, 2011, **50**, 3376-3410.
8. G. M. Lazzerini, G. M. Paternò, G. Tregnago, N. Treat, N. Stingelin, A. Yacoot, F. Cacialli, ***Applied Physics Letters***, 2016, **108**, 053303.
9. J. Park, C. Barolo, F. Sauvage, N. Barbero, C. Benzi, P. Quagliotto, S. Coluccia, D. Di Censo, M. Gratzel, M. K. Nazeeruddin, G. Viscardi, ***Chem Commun*** *(Camb)*, 2012, **48**, 2782-2784.
10. J. H. Yum, P. Walter, S. Huber, D. Rentsch, T. Geiger, F. Nuesch, F. De Angelis, M. Gratzel, M. K. Nazeeruddin, ***J Am Chem Soc***, 2007, **129**, 10320-10321.
11. S. Galliano, V. Novelli, N. Barbero, A. Smarra, G. Viscardi, R. Borrelli, F. Sauvage, C. Barolo, ***Energies***, 2016, **9**, 486.
12. J. S. Huang, T. Goh, X. K. Li, M. Y. Sfeir, E. A. Bielinski, S. Tomasulo, M. L. Lee, N. Hazari, A. D. Taylor, ***Nat Photonics***, 2013, **7**, 480-486.
13. G. Chen, H. Sasabe, T. Igarashi, Z. R. Hong, J. Kido, ***J Mater Chem A***, 2015, **3**, 14517-14534.
14. T. Kinoshita, K. Nonomura, N. J. Jeon, F. Giordano, A. Abate, S. Uchida, T. Kubo, S. I. Seok, M. K. Nazeeruddin, A. Hagfeldt, M. Gratzel, H. Segawa, ***Nat Commun***, 2015, **6**, 8834.
15. B. Stender, S. F. Volker, C. Lambert, J. Pflaum, ***Advanced materials***, 2013, **25**, 2943-2947.
16. L. Serpe, S. Ellena, N. Barbero, F. Foglietta, F. Prandini, M. P. Gallo, R. Levi, C. Barolo, R. Canaparo, S. Visentin, ***Eur J Med Chem***, 2016, **113**, 187-197.
17. R. R. Avirah, D. T. Jayaram, N. Adarsh, D. Ramaiah, ***Org Biomol Chem***, 2012, **10**, 911-920.
18. G. Chen H. Sasabe W. Lu X. F. Wang J. Kido Z. Hong, ***J Mater Chem C,*** 2013, **1**, 6547.
19. S. Spencer H. Hu Q. Li HY. Ahn M. Qaddoura M, S. Yao, ***Prog Photovoltaics Res Appl,*** 2014, **22**, 488–93.
20. F. Balzer H. Kollmann M. Schulz G. Schnakenburg A. Lützen M. Schmidtmann, ***Cryst Growth Des,*** 2017, **17**, 6455–66.
21. C. Zheng, A. R. Penmetcha, B. Cona, S. D, Spencer B. Zhu P. Heaphy, **Langmuir**, 2015, **31**, 7717–26.
22. K. C. Deing U. Mayerhoffer F. Wurthner, K. Meerholz, ***Phys Chem Chem Phys*** 2012, **14**, 8328–34.

23. O. P. Dimitriev, A. P. Dimitriyeva, A. I. Tolmachev, V. V. Kurdyukov, ***The journal of physical chemistry B***, 2005, **109**, 4561-4567.
24. P. Chithra, R. Varghese, K. P. Divya, A. Ajayaghosh, ***Chemistry, an Asian journal***, 2008, **3**, 1365-1373.
25. A. Ajayaghosh, P. Chithra, R. Varghese, K. P. Divya, ***Chem Commun*** *(Camb)*, 2008, **0**, 969-971.
26. B. Di Bartolo, *Spectroscopy of the excited state*, ***Springer Science & Business Media***, 2012.
27. C. Zheng, I. Jalan, P. Cost, K. Oliver, A. Gupta, S. Misture, J. A. Cody, C. J. Collison, J. ***Phys. Chem***. **C**, 2017 **12114**, 7750-7760
28. Y. Chen, L. Yang, J. Wu, G. Wang, W. Huang, F. S.Melkonyan**,** Z. Lu, Y. Huang, T. J. Marks**,** A. Facchetti, ***Chem. Mater***., 2018 **3019**, 6810-6820.
29. C. Zheng, C. Zhong, C. J. Collison, F. C. Spano, ***J. Phys. Chem. C***, 2019, **123(5)**, 3203-3215
30. M. Gsänger , D. Bialas , L. Huang , M. Stolte , F. Würthner, ***Adv. Mater.,*** 2016, **28**, 3615–3645.
31. C. Zheng, D. Bleier, I. Jalan, S. Pristash, A. R. Penmetcha, N. J. Hestand, F. C. Spano, M. S. Pierce, J. A. Cody, C. J. Collison, ***Solar Energy Materials and Solar Cells***, 2016, ***157***, 366-376.
32. N. J. Hestand, C. Zheng, A. R. Penmetcha, B. Cona, J. A. Cody, F. C. Spano, C. J. Collison, ***The Journal of Physical Chemistry C***, 2015, *119*(33), 18964-18974.
33. G. M. Paternò, L. Moretti, A. J., Barker, C. D'Andrea, A. Luzio, N. Barbero, S. Galliano, C. Barolo, G. Lanzani, F. Scotognella, ***Journal of Materials Chemistry C***, 2017, ***5*(31)**,7732-7738.
34. P. Wickramsinghe, P. Deokar, P. I. Djurovich, R. Haiges, R. M. E. Thompson, ***Journal of Photochemistry and Photobiology A*** *Chemistry*, 2019, *374*,16-21.
35. D. Yang, Y. Jiao, L. Yang, Y. Chen, S. Mizoi, Y. Huang, X. Pu, Z.. Lu, H. Sasabe, J. Kido, ***Journal of Materials Chemistry A*****,** 2015, ***3*(34)**, 17704-17712.
36. S. Brück, C. Krause, R. Turrisi, L. Beverina, S. Wilken, W. Saak, A. Lützen, H. Borchert, M. Schiek, J. Parisi, ***Physical Chemistry Chemical Physics***, 2014, ***16*(3)**, 1067-1077.
37. C. Zheng, L. Jalan, P. Cost, K. Oliver, A. Gupta, S. Misture, J. A. Cody, C. J. Collison, ***The Journal of Physical Chemistry C***, 2017, ***121*(14)**, 7750-7760.
38. F. Balzer, H. Kollmann, M. Schulz, G. Schnakenburg, A. Lützen, M. Schmidtmann, C. Lienau, M. Silies, Schiek, ***Crystal Growth & Design***, 2017, ***17*(12)**, 6455-6466.
39. D. Yang, T. Sano, H. Sasabe, L. Yang, S. Ohisa, Y. Chen, Y. Huang, J. Kido, ***ACS applied materials & interfaces***, 2018, ***10*(31)**, 26465-26472.
40. Q. Xiao, S. Yang, R. Wang, Y. Zhang, H. Zhang, H. Zhou, Z. A. Li, ***Dyes and Pigments***, 2018, ***154***, 137-144.
41. J. Wu, D. Yang, Q. Wang, L. Yang, H. Sasabe, T. Sano, J. Kido, Z. Lu, Y. Huang, ***Journal of Materials Chemistry A***, 2018, ***6*(14)**, 5797-5806.
42. M Gsänger, E. Kirchner, M. Stolte, C. Burschka, V. Stepanenko, J. Pflaum, F. Würthner, ***Journal of the American Chemical Society***, 2014, ***136*(6)**, pp.2351-2362.
43. G. H. Rao, P. J. S. Rana, P.K. Chitumalla, J. Jang, S. P. Singh, ***ACS Omega***, 2018, ***3*(11)**, 15416-15425.
44. S. Khopkar, S. Deshpande, G. Shankarling, ***Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*****,** 2019, ***211***, 114-124.
45. G. H. Rao, P. J. S. Rana, P.K. Chitumalla, J. Jang, S. P. Singh, ***ACS Omega***, 2018, ***3*(11)**, 15416-15425.
46. G. H. Rao, P. J. S. Rana, A. Islam, A. S. P. Singh, ***ACS Applied Energy Materials***, 2018, ***1*(9)**, 4786-4793.
47. R. Bisht, M F. Mele Kavungathodi, J. Nithyanandhan, ***Chemistry–A European Journal***, 2018**,** ***24*(61)**, 16368-16378.
48. R. Bisht, V. Sudhakar, M F. Mele Kavungathodi, N. Karjule, J. Nithyanandhan, ***ACS applied materials & interfaces***, 2018, ***10*(31),** 26335-26347.

49. V. Punitharasu, M F. Mele Kavungathodi, J. Nithyanandhan, ***ACS applied materials & interfaces***, 2018, *10*(19), 16541-16551.
50. T. Maeda, T. V. Nguyen, Y. Kuwano, X. Chen, K. Miyanaga, H. Nakazumi, S. Yagi, S. Soman, A. Ajayaghosh, ***J. Phys. Chem. C,*** 2018, **122 (38),** 21745-21754
51. V. V. Divya, C. H. Suresh, ***ChemistrySelect*** 2019, ***4***, 3387 –3394
52. S. Sanyal, A. Painelli, S. K. Pati, F. Terenziani, C. Sissa, ***Physical Chemistry Chemical Physics***, 2016, ***18*(40)**, 28198-28208.
53. Ch. Prabhakar, G. Krishna Chaitanya, S. Sitha, K. Bhanuprakash, V. J. Rao, ***J. Phys. Chem. A*** 2005, ***109****,* 2614-2622
54. Ch. Prabhakar, K. Yesudas, G. Krishna Chaitanya, S. Sitha, K. Bhanuprakash, V. J. Rao, ***J. Phys. Chem. A*** 2005, ***109****,* 8604-8616
55. K. Yesudas, G. Krishna Chaitanya, Ch. Prabhakar, K. Bhanuprakash, V. J. Rao, ***J. Phys. Chem. A*** 2006, ***110****,* 11717-11729
56. G. Krishna Chaitanya, A. L. Puyad, K. Bhanuprakash, **RSC Adv.,** 2015, **5**, 18813
57. G. Krishna Chaitanya, A. L. Puyad, K. Bhanuprakash**, Computational and Theoretical Chemistry**, 2017, **1118,** 123–132
58. A. L. Puyad, G. Krishna Chaitanya, A, Thomas, M. Paramasivam, K. Bhanuprakash, **J. Phys. Org. Chem.** 2013, **26,** 37–46
59. J. Park, C. Barolo, F. Sauvage, N. Barbero, C. Benzi, P. Quagliotto, S. Coluccia, D.D. Censo, M. Grätzel, M.K. Nazeeruddin, G. Viscardi, **Chem. Commun**., 2012, **48,** 2782–2784.
60. J. Park, N. Barbero, J. Yoon, E. Dell'Orto, S. Galliano, R. Borrelli, J.H. Yum, D.D. Censo, M. Grätzel, M.K. Nazeeruddin, C. Barolo, G. Viscardi, **Phys. Chem. Chem.Phys.**, 2014, **16,** 24173–24177.
61. L. Yang, D. Yang, Y. Chen, J. Wu, Z. Lu, H. Sasabe, J. Kido, T. Sano, Y. Huang, ***Mater. Chem. Front.***, 2018,**2**, 2116-2123
62. J. Wu, D. Yang, Q. Wang, L. Yang, H. Sasabe, T. Sano, J. Kido, Z. Lua, Y. Huang, ***J. Mater. Chem. A***, 2018,**6**, 5797-5806
63. A. L. Puyad, G. Krishna Chaitanya, Ch. Prabhakar, K. Bhanuprakash, **J Mol Model** , 2013**, 19**,275–287
64. A. Valaboju, G. Krishna Chaitanya, K. Bhanuprakash, D. Joly, M. Hissler, **Computational and Theoretical Chemistry**, 2017, **1113,** 61–71
65. G. Dhangar, J. L. Serrano, C. Schulzke, G. Krishna Chaitanya, A. R. Kapdi, **ACS Omega** 2017, **2**, 3144−3156
66. B. G. Ghule, S. Shaikh, S. U. Ekar, U. T. Nakate, G. Krishna Chaitanya, N. M. Shinde, Mu. Naushad, K. Ho Kim, C. O'Dwyer, R. S. Mane, **ACS Appl. Mater. Interfaces** 2017, **9**, 43051−43060

Research Scholar

Rupali R. Deshmukh

Ph.D. Supervisor

Dr. G Krishna Chaitanya

Associate Professor,

School of Chemical Sciences,

SRTMU, Nanded.